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Structural and Surface Modification of Carbon Nanotubes for Enhanced Hydrogen Storage Density

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Abstract

In this paper, we report the synthesis of functionalized carbon nanotubes (F-CNTs) by acid treatment and their hydrogen storage properties. These F-CNTs have been characterized by XRD, FTIR, Raman spectroscopy and electron microscopy techniques. The results show that the structure and morphology of P-CNTs have been modified after the acid treatment. The hydrogen storage capacity was determined by volumetric measurements at room temperature and experimental results showed that the storage capacities of P-CNTs and F-CNTs were 0.65 wt% and 0.89 wt%, respectively. A notable enhancement in hydrogen storage capacity of F-CNTs was observed which could be attributed to the enhanced oxygen functionalities, opening of end caps and presence of surface defects that offered enhanced surface area for hydrogen adsorption. The key results of present research show that structural, morphological and chemical changes are responsible factors to enhance the hydrogen storage density.

Keywords: Hydrogen storage, functionalized carbon nanotubes, chemical functionalization, adsorption, Raman spectroscopy.

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1. Introduction

The ever-increasing worldwide demand of energy consumption, as well as concern about shortage of non-renewable fossil fuels (petroleum, coal, oil and gas) and global warming has inspired scientific community to do intensive research to develop new alternative sustainable energy sources that can replace carbon based fossil fuels [1]. There are number of alternative energy sources such as solar, wind, ocean, geothermal and hydrogen [2]. Hydrogen is one of the potential green fuels because it is lightweight, eco-friendly, renewable, and four times more efficient than petroleum [3-4]. For the utilization of molecular hydrogen as energy carrier, its production, storage and transportation crucial. Hydrogen storage is one of the major challenges because hydrogen is present in the gaseous form in ambient condition. Hydrogen is the lightest gas in the atmosphere. Hydrogen gas can be stored as (i) pressurized gas, (ii) cryogenic liquid, (iii) solid fuel as chemical (metal hydrate) or physical combination (carbon material) [5]. All the storage methods are discussed in the following reviews [6-7]. The cryogenic hydrogen storage requires cryogenic unit to maintain the temperature that makes it an energy consuming process. The high pressure hydrogen storage requires high pressure and high mechanical strength piston pump. Although each of above storage methods have some advantages but none of them satisfy the size, efficiency, weight, and safety necessities for own transportation vehicle [8]. Solid fuel by means of physical combination in which hydrogen is physically bonded to the surface of potential materials is another alternative for hydrogen storage.

Carbon is one of the adsorbent for gases because these materials demonstrate unusual properties with highly spongy structure and the existence of specific interfaces among the carbon atoms and hydrogen gas [9-11]. The properties of carbon such as high mechanical strength, long life, efficient heat transfer coefficient, fast thermodynamically kinetics (quick uptake and release)

make it a desirable material for hydrogen storage. In addition, carbon materials have the advantage of being lighter than the inorganic compounds that are available in the market [12-14]. In 1991, Iijima et al. added a new member of carbon family, namely carbon nanotubes that have the ability of high hydrogen storage density [15]. The variety of carbon nanostructured materials, such as multi walled carbon nanotubes [10], single walled carbon nanotubes [11], graphene based derivative [14] and other varies carbon [13] materials have been investigated experimentally as well as theoretically for various energy applications including hydrogen storage**. For instance, ammonia boranes have received significant attention in recent years as a source of hydrogen [16]. Sen et al. have extensively investigated various carbon nanocomposite materials for hydrogen generation from ammonia boranes [17-20]. The novel carbon nanomaterials namely CNT, graphene and graphene oxidewere mixed with metallic and metallicalloy nanomaterials to prepare thenanocomposites [21, 22]. Ruthenium-cobalt alloy nanoparticles-functionalized MWCNTs (RuCo-FMWCNT) composites have been demonstrated to be the best catalyst for the dehydrogenation of dimethylamine borane (100% conversion, turn over frequency 775.28 h^{-1}) [23]. Carbon-metal composites have also been explored for other application including solar cell and organic synthesis [24, 25]**. Darkrim and Wang groups using computational methods proposed that the hydrogen molecules are absorbed by the carbon structure due to the Van der Waal's force on the surface of the material [26, 27]. Cheng et al. reported that storage capacity of carbon nanotube increases by the optimization of CNT diameter, inter-tube spacing and array configuration. They demonstrated that single walled carbon nanotubes can store more than 10.0 wt.% hydrogen at 298K and 10 MPa [28]. Carbon nanotube is one of the most interesting material due to their structural characteristics, such as high theoretical surface area, porosity,

high mechanical strength and durability, effective heat transfer, narrow pore size distribution and low mass density [29]. Durgun et al. studied the hydrogen storage capacity theoretically using first principle method and showed transition metals decorated carbon nanotube may bind multiple H_2 molecules which could be correlated with enhanced hydrogen storage capacity [30]. Zuttle et al. Experimentally investigated the hydrogen absorption through the surface of carbon nanotubes [31]. Hydrogen storage study has been carried out for CNT at 10.5 MP pressure is 0.7 wt.% [32] and in CNT film is 8 wt.% [33] at room temperature and ambient pressure. Recently, Reddy et al. [34] reported the platinum dispersion on single walled carbon nanotubes enhances the storage capacity. Gayathri et.al. have been studied the H_2 adsorption in defected CNTs and reported that hydrogen can be adsorbed on carbon nanotube in two manners physical adsorption and chemisorption [35]. Interconnected carbon nanotubes (CNT) composed a newly diamond-like architecture namely super diamond. It has been designed by tunable pores and controlling the location of defects. The hydrogen storage properties were studied thoroughly via ab-initio and Grand Canonical Monte Carlo simulations and results showed the gravimetric capacity of 20% at 77 K and can reach the high value of 8% at room temperature [36]. Sharma et al. Showed a comparative study of hydrogen storage capacity of GO and Go-PANI nanocomposite and reported the GO-PANI nanocomposite has low storage capacity in comparison to GO [37]. Interlayer spacing, functional group and defect density also play a major for enhance the hydrogen storage density [38, 28].

Yildrim etal.studied the hydrogen storage capacity theoretically and predict the functionalized the carbon nanotube with Sc, V and Ti holds high theoretical gravimetric densities of 9.8, 9.2 and 7.8 wt.% respectively [39]. However, Liu et al. reported the 2.9wt.% hydrogen storage capacity of hybrid GO-MWCNTs nanocomposites[40]. Ruoff

etal.synthesized the graphene like nanosheets reduction of exfoliated graphite and studied the hydrogen storage behavior [41]. Similarly, Kim et al. thermally reduced the graphene oxide, note the hydrogen storage capacity, and explore the functional group play a major role to enhance the hydrogen storage [42]. Rao et. al study the effect of acid treatment of CNTs and their hydrogen storage behavior [43]. Cheng et al. activated CNT via various chemical and physical techniques and report the opening the defective siteand surface modification after activation a major way to enhance the modified carbon nanotubes [44]. Nanostructure graphite was prepared by mechanical milling under hydrogen atmosphere and the hydrogen storage performance was recorded [45]. A high hydrogen storage capacity of graphene, nitrogen–doped graphene and Pd decorated nitrogen-doped hydrogen exfoliated graphene nanocomposite is demonstrated under moderate temperature and pressure conditions [46]. High-pressure hydrogen sorption isotherms were investigated on by thermally reduced GP (TR-GO), chemically reduced GO (CR-GO) and graphene sheets decorated with Fe nanoclusters (Fe-GS) [47]. Li and K doped CNTs can hold 20 wt % and 14 wt.% hydrogen at moderate or room temperatures, respectively, under ambient pressure [48].The high hydrogen-uptake capacity of these systems may be derived from the special open-edged, layered structure of the carbon nanotubes and used carbon precursor source and catalysis. G. E. Froudakis et al. investigate the hydrogen storage capacity in silicon –carbon nanotube using Ab initio simulation and report the hydrogen storsge capacity 3.6 wt% at high pressure [49]. M. Rodriguez et al synthesis the graphite nanofiber by dissociation of carbon containing gas on metal surface and synthesis the graphite nanofiber and report the hydrogen storage behavior [50]. The earlier

reported hydrogen uptake capacity and some related parameters of carbon nanostructures have been summarized in table 1.

Many reports stated above used more than one-step for the activation of CNTs for hydrogen storage. Aiming towards simple activation procedure for CNTs, current research focus on enhancing the hydrogen storage density economically in graphene based derivatives. The activation can be achieved from different chemical and physical techniques, which results in increasing porosity, active sites, interlayer spacing and defects in the structure [51-52]. CNTs activation by acid treatment for hydrogen storage is a relatively a new approach with limited studies. In this paper, we are reporting, simple modification of P-CNTs using the chemical oxidation method and investigated the hydrogen storage properties.

2. Experimental section

2.1. Synthesis of F-CNTs

The P-CNTs were purchased from the Redux Private Ltd. India. The P-CNTs were 10-30 μm long with outside diameter 2-30 nm having purity level 95%. Concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3) were purchased from Sigma-Aldrich. The CNTs were functionalized by the well-known chemical oxidation method [53-54]. In brief, a molar ratio of 3:1 H_2SO_4 and HNO_3 solution was added to P-CNTs powder under ultra-sonication for 2 h. The resultant solution was stirred at temperature 80°C for 24 h. The solution was dried in vacuum oven followed by centrifugation at 4000 rpm and the resultant pellet was collected. The overall synthesis procedure of F-CNTs is shown in figure 1.

2.2. Characterization techniques

Transmission electron microscope (TEM, Tecnai G20 S-TWIN) was carried out 200 kV bias. Scanning electron microscope (SEM) analysis was then carried out using Carl Zeiss EVO 18 at 20 kV operating voltage. The X-ray diffractogram (XRD) was recorded using PanalyticalX'pert PRO MPD system using Cu K_α X-ray source. Raman spectra were recorded on the R-3000 Raman Systems with 514.5 nm Ar laser source. FTIR spectra were recorded using Shimadzu IR Affinity-1 FTIR spectrometer.

2.3. Hydrogen storage Setup

The hydrogen storage properties of the samples were investigated in a custom build hydrogen storage setup at room temperature as shown in figure 2. The known amount of the materials was kept in the stainless-steel chamber and the setup was completely degassed for 30 minutes using rotary vacuum before any measurements. In the next step, particular pressures (for instance 80 bar) of ultra-pure hydrogen were introduced followed by the measurements of pressure drop with time. The measurements were repeated six times and average values have been reported in the paper [55].

3. Results and discussions

3.1. Morphology

The surface morphology of P-CNTs and F-CNTs were determined by SEM. Figure 3(a) shows the SEM image of agglomerated rough 3D structure of P-CNTs with intricate network of interconnected fiber-like structures. The acid treatment prevented the bundling and agglomeration of CNT fibers. As shown in figure 3(b), F-CNTs have increased intermediate

spaces and groove openings. For further structural evidences, TEM analysis was performed for CNTs before and after of acid treatment [56].

Bright filed TEM image of P-CNTs figure 4(a) exhibits an inhomogeneous complex network of interconnected ropes like structure. This snowflake type uneven structure is usually good material for hydrogen storage [57]. But P-CNTs are not so capable of storing hydrogen enormously when compared to the functionalized forms of CNTs. The Low storage density of hydrogen in P-CNTs is due to the deficiency of oxygen functionalities and defect free surface that obstruct or abandon the adsorption of hydrogen on the surface of the P-CNTs. Therefore, functionalization overcomes the stated difficulties and helps in increased hydrogen efficiency. In this study, F-CNTs are synthesis after acid treatment and the TEM image of F-CNTs are shown in figure 4(b-f). The image 4(b) are showing a tree branch like structure aligned together which reveal comparatively rough surface for hydrogen storage after the functionalization. It also demonstrates the outside wall of the tube has been damage (black arrow line) through the oxidization of CNTs. This evidence is a direct proof of surface modification where we can observe the newly created defects in F-CNTs after oxidative treatment. The closer investigation in figure 4(c) shows the opening end cap of F-CNTs after chemical oxidation. This may attribute to additional attachment of oxygen functionalities and improves the storage efficiency of F-CNTs. Figure 4 (d) shows that defect on surface of CNTs that specify the white circle area which had introduced the hydrogen friendly active sites on surface of F-CNTs. The high-resolution image in figure 4(e-f) of shows the exact minuscule structure CNTs before and after of chemical oxidation. The darker line that is marked by white arrow line, which might be edge of graphene sheet are clearly visible in figure 4(e). This lattice fringe displaying interatomic interlayer spacing of F-CNTs is 0.34 nm. After the chemical oxidation of P-CNTs, edge of graphene layer

is partially destroyed, not well arranged, and poor crystalline with destructive surface morphology were also observed in figure 4(f). Similarly, result has been reported [58, 59] that chemical and physically modified could cause the defect on surface of CNTs.

3.2. X-ray diffraction analysis

The crystalline structure of P-CNTs and F-CNTs were studied by X-Ray diffraction shown in the figure 5. X-ray diffraction (XRD) has proved a useful tool to characterize the crystal structures and atomic spacing of CNTs. The high intensity peaks in XRD pattern of P-CNTs, black line, appear at angle of 25.7^0 (002) conforming the interlayer distance 0.34 nm to significantly good nanotubes orientation [60]. The peaks at about 43° and 53° are due to C(100) and C(004), respectively. The other peaks are believed to be due to the contamination. It is a simple approach to analysis the alignment of P-CNTs without destructing with their original alignment. The most intense peak of F-CNTs, red line, sheets appear at 2θ of 25.5□ corresponding to the interlayer spacing 0.35 nm. This facilitates to attachment of oxygen functional groups via strong acid treatment, which confirms the disturbance in the alignment of carbon nanotubes and increase in the inter-layer distance in between the graphene layers that is new propitious for enhance hydrogen storage density [61]. This result is further confirmed by the Raman spectroscopy measurements.

3.3. Spectroscopic analysis

Raman spectroscopy is highly sensitive to analysis the electronic structure of carbon nanostructure materials. It is important technique to analysis the single, double and multi wall of

carbon nanotube. The Raman spectra of the P-CNTs and F-CNTs are shown in figure 6. The P-CNTs show the three prominated peaks are located at 1325, 1580 and 2644 cm^{-1} are shifted to F-CNTs at 1347, 1599, 2683 cm^{-1} [62, 63]. The first peak is known as the D band, which is originated due to breathing mode of sp^2-hybridization, and disorder structure in CNTs. The intensity of the D band is directly relative to the amount of defects in the sample. Second peak is called the G band, which is appearing due to in-plane vibration of sp^2 carbon atoms and it is common for all sp^2 carbon systems. Third peak is known as 2D band (historically know as G' band) that is originates from a process where two phonons with opposite momentum exchange occurs and it is overture of D band. The position and shape of 2D band is highly sensitive to determine the thickness and number of layer of graphitic materials. However, in process of F-CNTs, the density of defect has been influence by acid treatment, that's via intensity of the 2D band decrease that is good agreements of previous publishing results [64, 65]. Further, the measuring the intensity ratio of D band and G band, we can get of information of disorder of F-CNTs. As shown in the figure P-CNTs have the intensity ratio (I_D/I_G) of 0.284 and after acid treatment F-CNTs show the higher intensity ratio of 0.433. The high intensity ratio of F-CNTs can be attributed to the activate the various defective cavities and defect on the graphene edge along the tube as well as attachment functional group on F-CNTs surface; this outcome is consistent with our TEM observation. Finally, Raman spectra show the acid treatment looks to more effective in creation of defect on surface which leads to enrich the storage density in F-CNTs.

The FTIR spectroscopy was used to confirm the functional group finding process in the sample. Specific functionalities of carbonyl and hydroxyl groups should be present in the product. Figure 7 illustrates the FTIR spectra of P-CNTs and F-CNTs. The broad peaks at 3414 cm^{-1} and small

peak 1333 cm^{-1} were observed for F-CNTs, it was attributed to the symmetric and asymmetric vibrations of -OH, indicating the acid treatment has successfully occurred on CNTs. The another peaks of oxygen functionalities located at 1090 cm^{-1} and 1632 cm^{-1} are corresponding to C–O (epoxy or alkoxy), and C=O carboxylic acid, respectively that are suggest the complicate oxidation has been successful on Pristine carbon nanotube after chemical oxidation method [66].

3.4. Hydrogen storage performance

The hydrogen storage measurements were carried out at high pressure and room temperature. The sketch of hydrogen adsorption uptake for P-CNTs and F-CNTs are shown in figure 8. The result shows that hydrogen uptake in F-CNTs has higher storage capability to P-CNTs. The P-CNTs a slightly adsorbed low amount of hydrogen 0.65 wt.% at 80 bar pressure. However, hydrogen uptake capacity increased in F-CNTs i.e., 0.89 wt%. at same pressure.

There are four possibilities for the reason for H_2 uptake on the carbon nanotube: (1) Inside the carbon nanotubes, (2) surface of the carbon nanotubes, (3) Channel of carbon nanotubes and (4) Grove of carbon nanotubes. The way and adsorption sites of hydrogen in carbon nanotubes bundles are shown diagrammatically in figure 9 [67].

The increase (~37 %) in H_2 uptake capacity of F-CNTs as compared to the P-CNTs can therefore be attributed to the attachment of functional group on the surface as described in FTIR section in figure 7, which clues to rise the inter layer space in between the graphene layer, increase porosity, and generate more reactive surface sites on surface of F-CNTs for enhance of hydrogen adsorption. Our results correlate with a reported study of Patchkovskii*et al*. [68] where the authors proposed that the hydrogen can be stored in

between inter layers of graphene. They also investigated the hydrogen storage capacity of graphene layer bycomputations simulation, and displayed that the interlayer distance plays a key role on hydrogen storage capacity. Furthermore, Lee, S.Y et al. also reported that the chemically modified CNTs are having high storage density when compared to P-CNTs. This is due to the oxygen functional on their surface, which provides more hydrogen-related surface sites [69]. The strong acid treatment of P-CNTs followed by attachment of functional group can create the defects on surface that are match with Raman spectra in figure 6 which might be another region enhancement of hydrogen storage in F-CNTs. Some research groups where they had modified CNTs with chemical treatment and by varying temperatures and they found that the modified P-CNTs have high storage density to un-modified also identified the same behavior. The defect structure on surface may be considered as significant factor to enrich hydrogen storage in modified carbon nanotubes [70, 71]. The appearing topological defect on the surface F-CNTs, which have been introduce hydrogen approachable active site by changing the characteristics of P-CNTs that offered the high attraction force for hydrogen molecules and carbon atom, which caused enhance the hydrogen storage density. As absorbed TEM image in figure 4(b, d) the defect on F-CNTs have been newly created and destructive surface morphology are forms after the acid treatment. It proposed that the enrich hydrogen storage in F-CNTs due to introduce the defect and open the end cap of CNTs, that are match with in TEM image figure 4(c). The simulation study shows the same finding and they have reported the introduction of the defects on surface can increase the local surface area, which can be, enhance the hydrogen storage density. The study suggests that graphene based derivative can be defect – engineering to develop an effective storage media. [72-74]. Our results show that the

engineering of the nanotubes surface and capped regions, nanotubes diameter, defect density, interlayer spacing and the surface functionalization group are effective in determination of the hydrogen storage capacity of the material.

4. Conclusions

In summary, the carbon nanotubes were functionalized using the chemical oxidation method. The hydrogen storage performance of P-CNTs and F-CNTs was determined at room temperature and high pressure using volumetric hydrogen storage system. The hydrogen uptake capacity for P-CNTs and F-CNTs at room temperature was measured to be 0.65 wt.% and 0.89 wt.%, respectively. The result shows that this considerable (~37%) enhancement in the storage capacity of F-CNTs is due to occurrence of large number of oxygen functionalities and high defect density that provide more reactive surface sites for adsorption of hydrogen on the surface of F-CNTs. Thus, this single step modification of P-CNTs in F-CNTs is an excellent option to enhance the hydrogen storage properties.

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Table Caption

Table 1 Summary of hydrogen storage studies of various carbon nanostructure materials.

Figure Caption:

Figure 1 Overall Synthesis procedure of F-CNTs.

Figure 2 Schematic diagram of volumetric hydrogen storage system.

Figure 3 SEM images of P-CNTs (b) and F-CNTs(c). Image (b) is showing the highly agglomeration interconnected fiber. Image (c) is showing the morphology of F-CNTs was disturbed after acid treatment.

Figure 4 Bright field TEM images of P-CNTs (a and its insert) and image (b-f) is F-CNTs. Scale bar of figure (a) insert is 50 nm. In image (b), black arrow indicate the side wall of F-CNTs has been damage and image (c) is showing the open the end cap of F-CNTs Image (d) showing defect on surface and white arrow line in image (e) is showing the edge of graphene. Image (f) is showing edge of graphene layer is partially destroyed.

Figure 5 XRD patterns of P-CNTs and F-CNTs.

Figure 6 Raman spectra of P-CNTs and F-CNTs.

Figure 7 FTIR spectra of P-CNTs and F-CNTs.

Figure 8 Hydrogen uptakes by P-CNTs and F-CNT at 80bars.

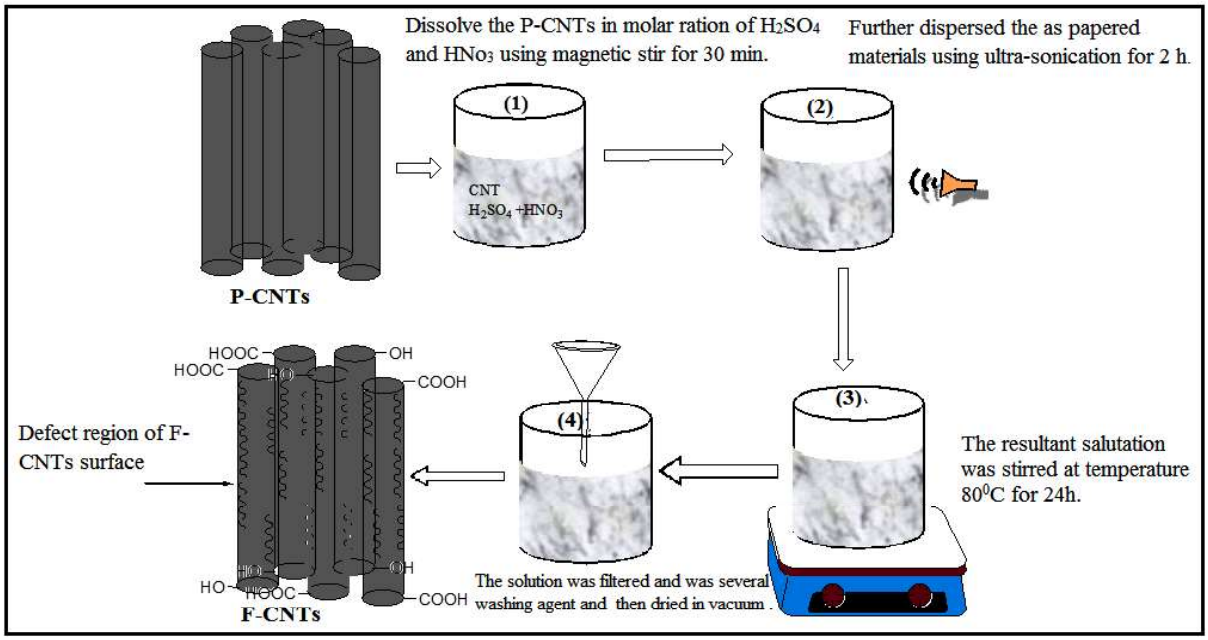
Figure 9 different storage sites of carbon nanotubes.

Table 1

Structured	**Binding Energy** $E_b(H_2)$	**Condition** (Temperature and Pressure)	**Wt %**	**Desorption Temperature** (T_D)	**Reference**
Carbon nanofiber	-	295 K, 105 bar	0.7	-	32
CNT thin film	-	Room temperature, Ambient pressure	8	-	33
CNT based three dimensional diamond like architecture	-	Room temperature	8	-	36
Sc-functionalized Graphene	0.17	-	8.0	391K	39
Sc- functionalized SWCNT	0.47	-	8.0 -9.8	733 K	39
V-Graphene functionalize	0.32	-	7.5	570 K	39
V- functionalized SWCNT	0.46	-	9.2	672 K	39
Ti-functionalized Graphene	0.35	-	7.8	611 K	39
Ti- functionalized SWCNT	0.56	-	5.3-7.8	867 K	39
Graphene Oxide-Multiwall Carbon Nanotube	-	298 K, 50 bar		-	40
Reduced Graphene Oxide Multiwalled Carbon Nanotube	-	298 K, 50 bar	2.1	-	40
Graphene like nanomaterils		298 K , 10 bar	1.2		41
Thermally modulated multilayered graphene oxide	-	298 K, 90 bar	0.5	-	42
Acid treated carbon nanotube	-	300 K, 143 bar	3.7	-	43
Air-oxidized MWCNTs	-	20.1K, 125 bar	0.9	-	44
CO2-oxidized MWCNT	-	20.1 K, 125 bar	1	-	44

KOH-activated MWCNTs	-	19.9 K, 120 bar	0.156	-	44
Nano-structured graphite	-	300 K, 10 bar	7.4		45
Pd decorated nitrogen doped graphene		298 K , 40 bar	4.4		46
Pd decorated graphene		298 K , 40 bar	1.47		46
Nitrogen doped graphene		298 K , 40 bar	0.81		46
Graphene oxide		300 K, 50 bar	0.17		47
Thermaly reduced graphene oxide		300 K , 50 bar	0.32		47
Chemically reduced graphene oxide		300 K , 50 bar	1		47
Fe decorated Graphene nanosheets		77 K , 50 bar			47
Li doped MWNT	-	200-400 K, 1 bar	20	-	48
K doped MWNT	-	200-400 K, 1 bar	14	-	48
Silicon−carbon nanotubes	-	175 K, 100 bar	3.68	-	49

Figure 1


Dissolve the P-CNTs in molar ration of H_2SO_4 and HNo_3 using magnetic stir for 30 min.
Further dispersed the as papered materials using ultra-sonication for 2 h.
(1)
CNT
H_2SO_4 +HNO_3
(2)
P-CNTs
HOOC
HOOC
OH
COOH
Defect region of F-CNTs surface
(4)
(3)
The resultant salutation was stirred at temperature 80^0C for 24h.
The solution was filtered and was several washing agent and then dried in vacuum .
HO
HOOC
OH
COOH
F-CNTs

.

Figure 2

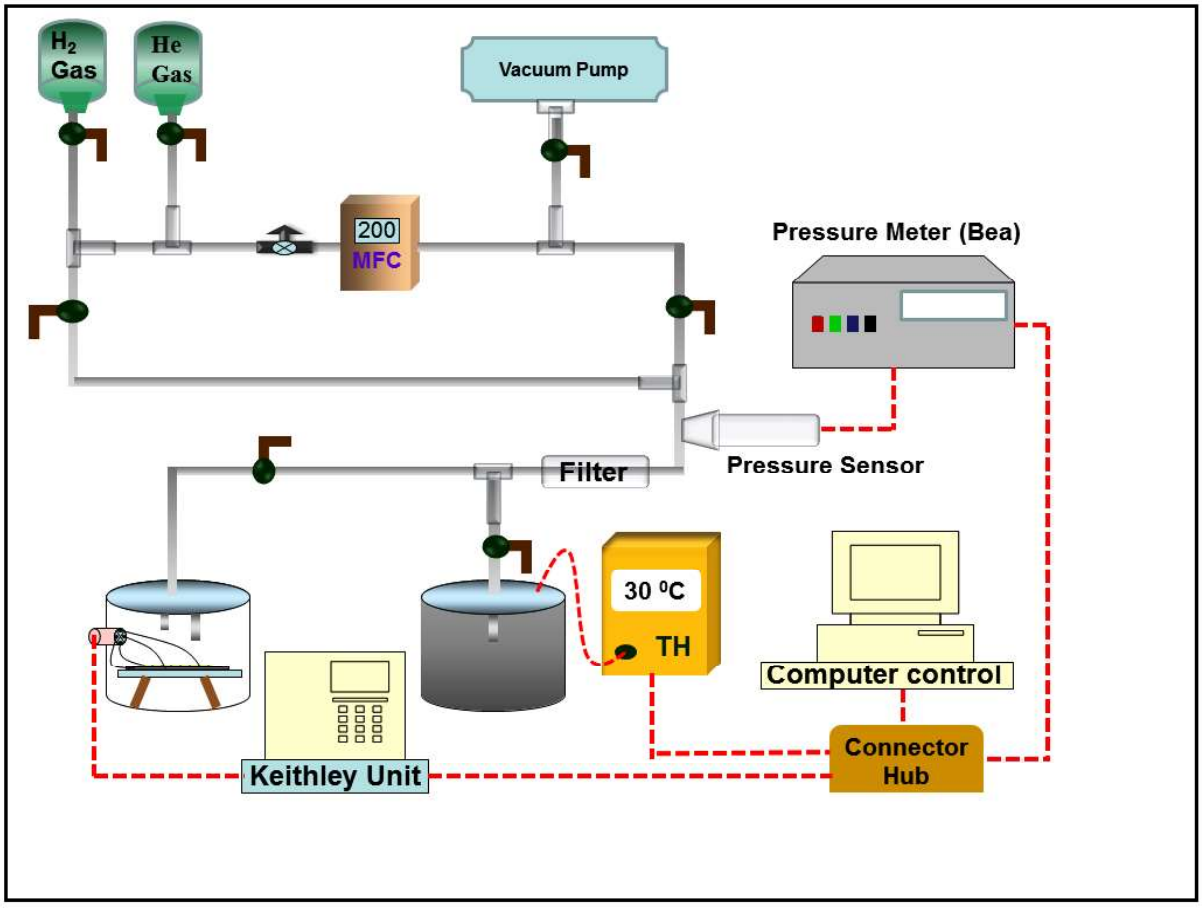

H2 Gas
He Gas
Vacuum Pump
200
MFC
Pressure Meter (Bea)
Pressure Sensor
Filter
30 °C
TH
Computer control
Keithley Unit
Connector Hub

Figure 3

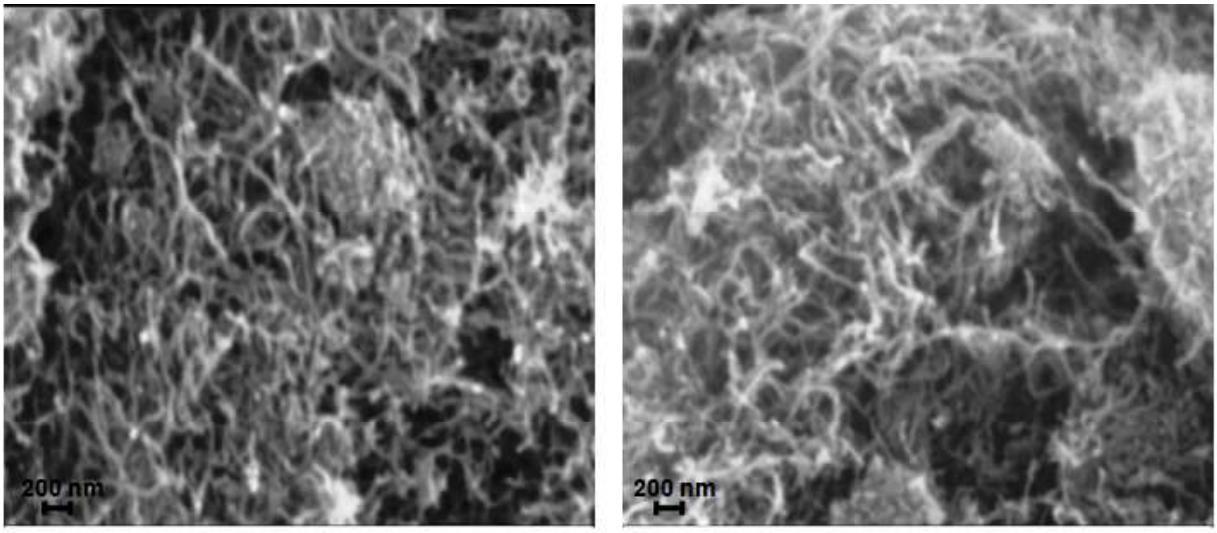


Figure-4

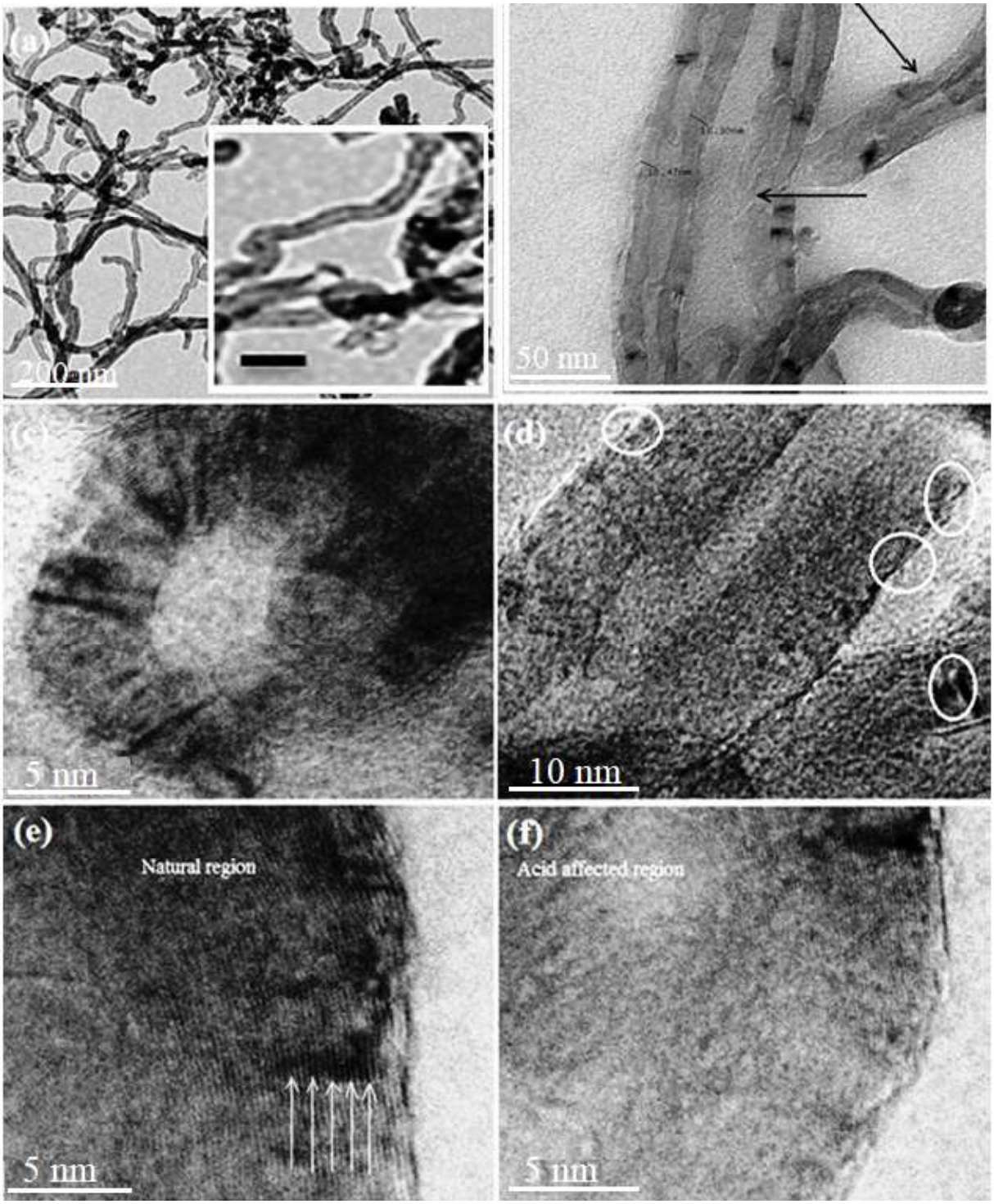

(a)
200 nm
50 nm
5 nm
(d)
10 nm
(e)
Natural region
5 nm
(f)
Acid affected region
5 nm

Figure 5

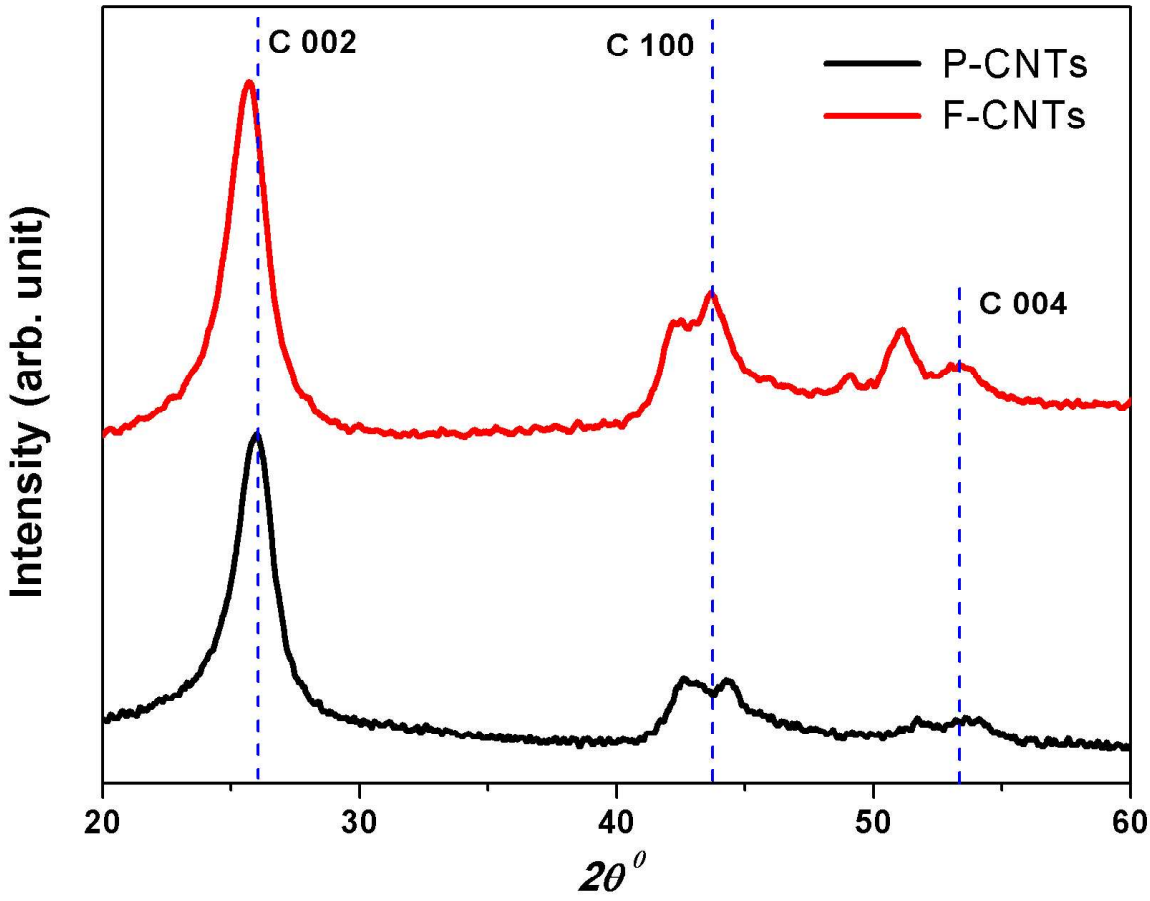

C 002
C 100
C 004
P-CNTs
F-CNTs
Intensity (arb. unit)
20
30
40
50
60
2θ⁰

Figure 6

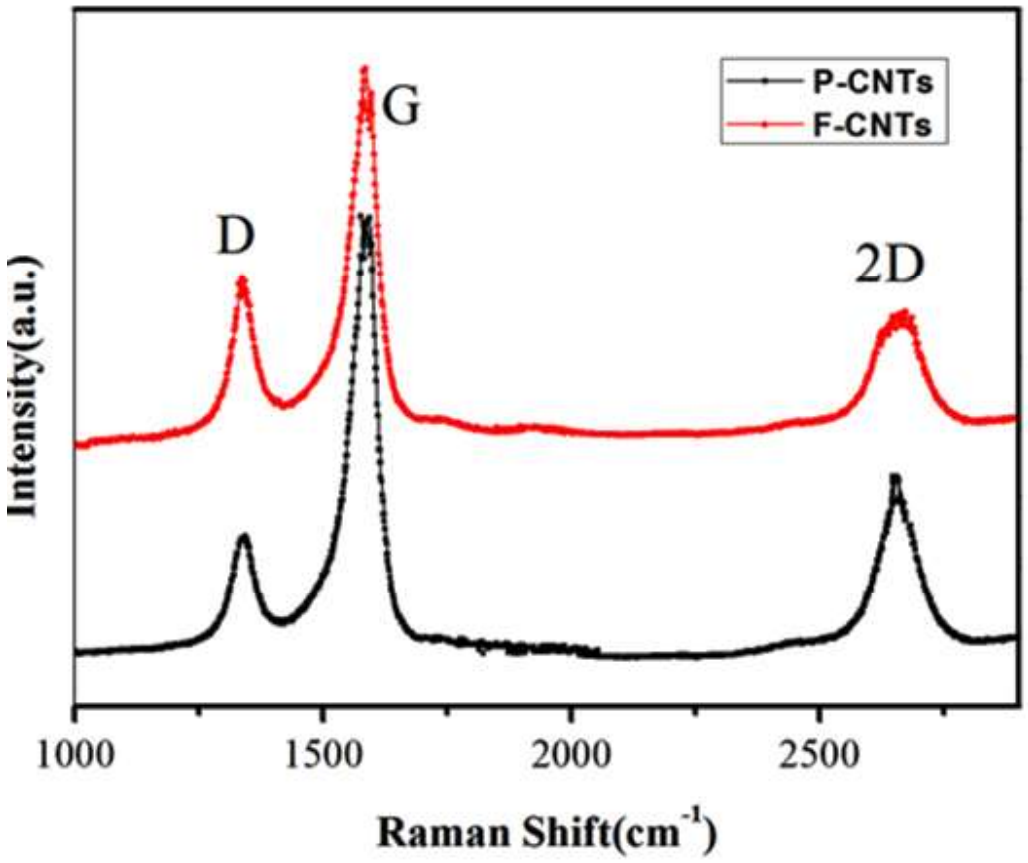

P-CNTs
F-CNTs
G
D
2D
Intensity(a.u.)
1000
1500
2000
2500
Raman Shift(cm-1)

Figure 7

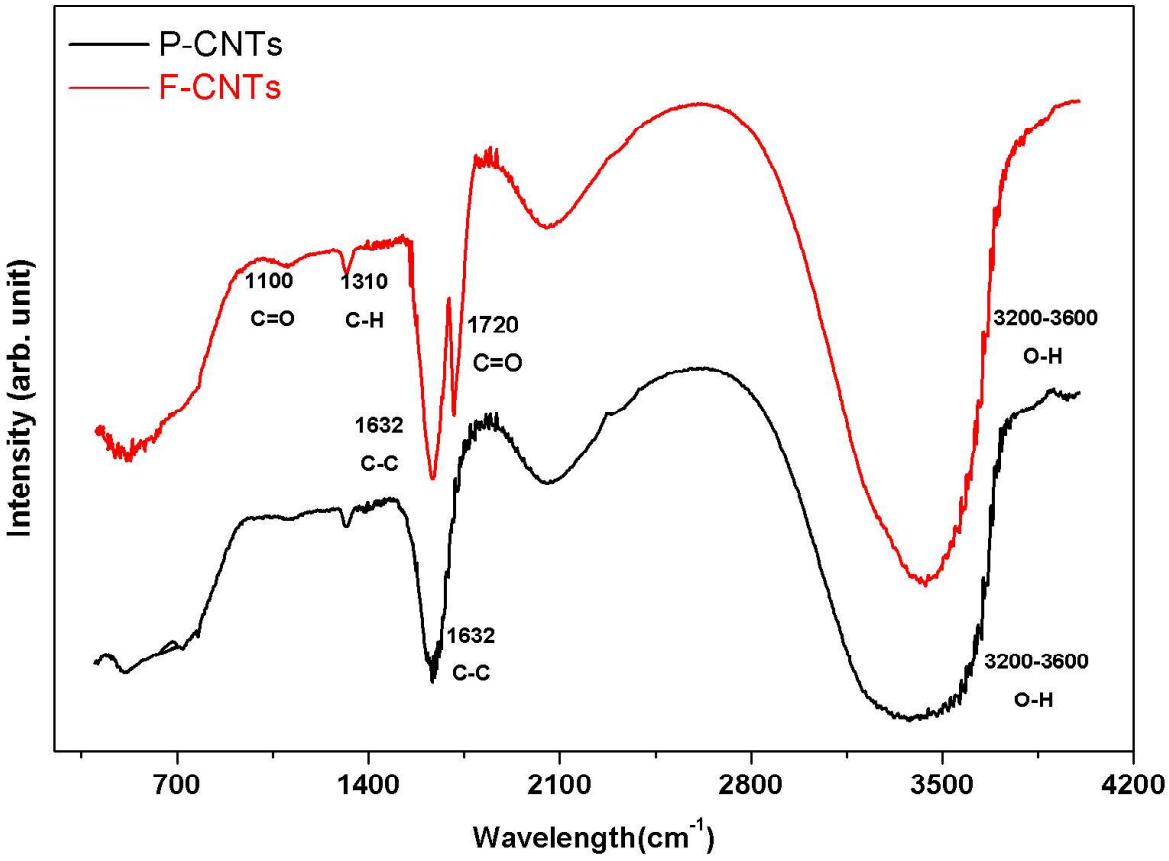

P-CNTs
F-CNTs
1100
C=O
1310
C-H
1720
C=O
3200-3600
O-H
1632
C-C
1632
C-C
3200-3600
O-H
Intensity (arb. unit)
700
1400
2100
2800
3500
4200
Wavelength(cm-1)

Figure 8

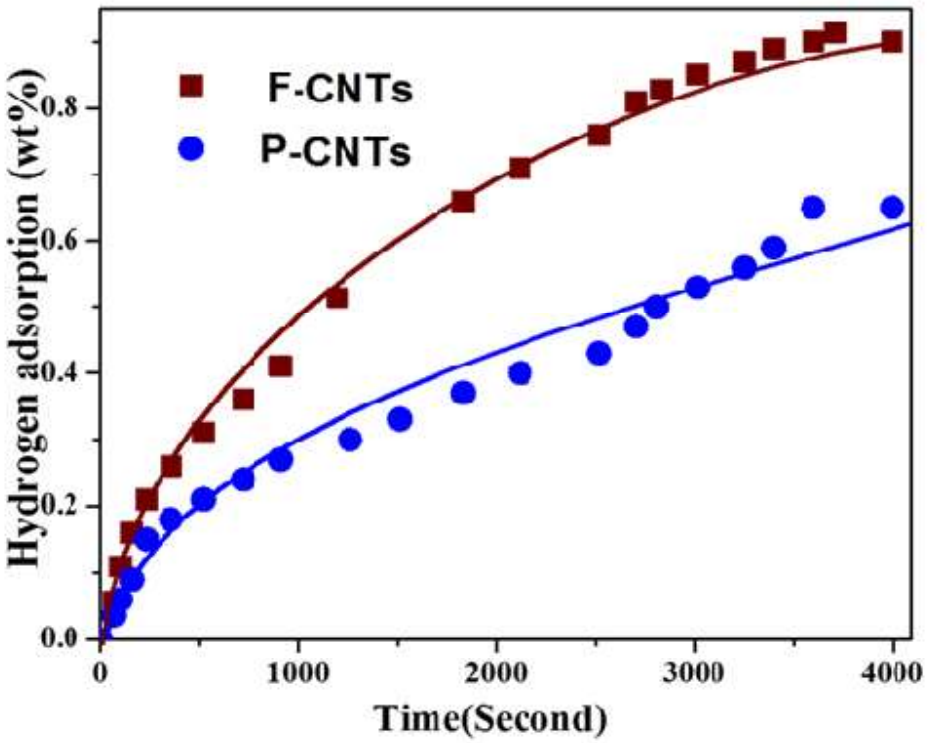
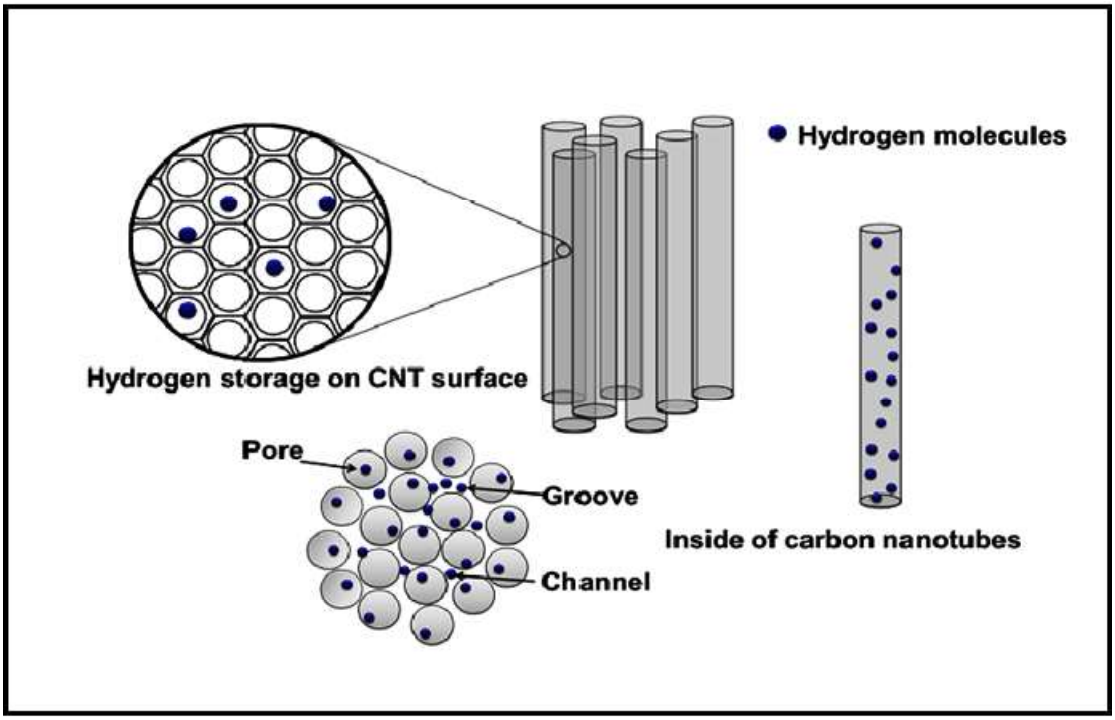

F-CNTs
P-CNTs
Hydrogen adsorption (wt%)
0.0
0.2
0.4
0.6
0.8
0
1000
2000
3000
4000
Time(Second)

Figure 9


Hydrogen molecules
Hydrogen storage on CNT surface
Pore
Groove
Channel
Inside of carbon nanotubes